

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the INPIT, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

1. Untranslatable words are replaced with asterisks (***).
2. Texts in the figures are not translated and shown as it is.

Translated: 21:46:31 JST 09/10/2009

Dictionary: Last updated 08/17/2009 / Priority:

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1]In blowing carbon dioxide into calcium hydroxide water suspension liquid, and manufacturing calcium carbonate, a substance which makes at least ** a metal ion and forms a complex in calcium hydroxide water suspension liquid is added, A manufacturing method of microscopic-particles calcium carbonate a carbonic acid-ized reaction's generating calcium carbonate and ripening this calcium carbonate after an appropriate time.

[Claim 2]A substance which makes at least ** a metal ion and forms a complex Hydroxycarboxylic acid, The manufacturing method according to claim 1 which is at least one sort chosen from poly hydroxycarboxylic acid, amino polycarboxylic acid, polyphosphoric acid, amino acid, those alkali metal salt, alkaline-earth-metals salt, ammonium salt, and a group that becomes from ketone.

[Claim 3]In hydroxycarboxylic acid, citrate, oxalic acid or malic acid, and poly hydroxycarboxylic acid Gluconic acid or tartaric acid, Amino polycarboxylic acid Iminodiacetate, ethylenediaminetetraacetic acid, or NITORIOTORI acetic acid, The manufacturing method according to claim 2 whose glutamic acid or aspartic acid, and ketone HEKISAMETA phosphoric acid or Tripoli phosphoric acid, and amino acid is ASECHIRU acetone, methyl acetoacetate, or aceto allyl acetate in polyphosphoric acid.

[Claim 4]The manufacturing method according to claim 1 which adds a substance which forms a complex which made at least ** a metal ion 0.1 to 10weight % to calcium hydroxide.

[Claim 5]The manufacturing method according to claim 1 which adds and ripens a phosphorus content substance to generated calcium carbonate slurry.

[Claim 6]The manufacturing method according to claim 5 which adds a phosphorus content substance 0.01 to 0.6weight % to calcium carbonate.

[Claim 7]The manufacturing method according to claim 5 or 6 which is at least one sort as which a phosphorus content substance is chosen from a group which consists of phosphoric

acid, phosphorous acid, phosphonic acid and those derivatives, those alkali metal salt, alkaline-earth-metals salt, and ammonium salt.

[Claim 8]The manufacturing method according to claim 1 with which in calcium hydroxide water suspension liquid concentration reaction start temperature carries out at 8-30 °C to 19.3%, and a carbon dioxide flow performs a carbonic acid-ized reaction under conditions of 40 per kg of calcium hydroxide - 1800 L/hr.

[Claim 9]The manufacturing method according to claim 1 which ripens by wet milling, ultrasonic dispersion, or churning at temperature of 20-70 °C.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is detailed, and there are few secondary aggregations, and it relates to the manufacturing method of good charcoal Cal made from sedimentation of dispersibility.

[0002]

[Description of the Prior Art]Now, as an industrial manufacturing method of the calcium carbonate made from sedimentation, the carbon dioxide method is adopted widely. Thus, in order to raise the physical properties at the time of combination further according to the size of the primary particle, the surface treatment of the manufactured calcium carbonate is carried out to a particle surface in various finishing agents of inorganic matter or an organic system, it is blended with rubber, a plastic, paper, a paint, etc., and is used in large quantities widely. However, originally, the calcium carbonate made from sedimentation manufactured by these carbon dioxide method has the strong cohesive force between particles, and many primary particles condense it and it forms the big secondary aggregation object.

It is made impossible to abolish a secondary aggregation object, maintaining the early diameter of a primary particle, even if the cohesive force of the diameter of a primary particle was strong about especially a thing of 0.2 micrometer or less and it used great energy especially.

[0003][the calcium carbonate made from sedimentation containing much such secondary aggregation objects] When it blends with rubber, a plastic, paper, a paint, etc., like a primary particle with big secondary aggregation particles, an action is carried out, the physical-properties fall of distributed [poor], strength reduction, a gloss fall, viscous shortage, etc. is caused, and various combination effects expected to a primary particle detailed originally are not acquired. Even if similarly it carries out the surface treatment of various finishing agents of inorganic matter or an organic system to the calcium carbonate made from sedimentation

containing much such secondary aggregation objects, the surface treatment of the secondary aggregation particles is only carried out, and sufficient effect is not demonstrated.

[0004]In order to distribute these secondary aggregation objects from the former, the process which ripens calcium carbonate slurry under conditions, such as warming and churning, is used. However, in this dispersion method, it becomes particles several times the size of even if a primary particle grows with advance of distribution of each particle. That is, in the distributed process by maturing, it is opposite phenomena to maintain the detailed diameter of a primary particle immediately after completing a carbonic acid-ized reaction and to distribute these condensation objects. As mentioned above, in conventional technology, it was impossible to have acquired the dispersion state near a primary particle as much as possible, while it has been in the particulate state where the use is expected widely industrially.

[0005]

[Problem to be solved by the invention]This invention is a manufacturing method which obtains the calcium carbonate whose dispersibility it is more detailed than the conventional calcium carbonate made from sedimentation, and is good in view of this actual condition. That is, in order to distribute the agglomerated particle of calcium carbonate, even if it uses the same maturing process as the former, the manufacturing method of the microscopic-particles calcium carbonate made into a good dispersion state will be provided, without growing up a primary particle as much as possible.

[0006]

[Means for solving problem]This invention persons found out wholeheartedly the manufacturing method of the calcium carbonate made from sedimentation whose dispersibility is detailed and good by adding a specific substance and performing a carbonic acid-ized reaction as a result of examination, in order to solve the above-mentioned technical problem. Namely, this invention blows carbon dioxide into calcium hydroxide water suspension liquid (it is hereafter described as milk of lime), and are in charge of manufacturing calcium carbonate, The substance (it is hereafter described as a complex morphogenetic substance) which makes at least ** a metal ion and forms a complex in calcium hydroxide water suspension liquid is added, a carbonic acid-ized reaction generates calcium carbonate, and the manufacturing method of the microscopic-particles calcium carbonate ripening this calcium carbonate after an appropriate time is made into the contents.

[0007]Below, the manufacturing method of this invention is explained more concretely. Milk-of-lime concentration adds a complex morphogenetic substance to 6.1 to 13.3% of milk of lime preferably 3.5 to 19.3% (it is below the sameweight %).

[0008]As a complex morphogenetic substance used for this invention, hydroxycarboxylic acid and its alkali metal salt, such as citrate, oxalic acid, and malic acid, Alkaline-earth-metals salt and ammonium salt; Poly hydroxycarboxylic acid and its alkali metal salt, such as gluconic acid

and tartaric acid, Alkaline-earth-metals salt and ammonium salt; Iminodiacetate, ethylenediaminetetraacetic acid, Amino polycarboxylic acid and its alkali metal salt, such as NITORIOTORI acetic acid, Alkaline-earth-metals salt and ammonium salt; Polyphosphoric acid and its alkali metal salt, such as HEKISAMETA phosphoric acid and Tripoli phosphoric acid, Alkaline-earth-metals salt and ammonium salt; Amino acid and its alkali metal salt, such as glutamic acid and aspartic acid, Alkaline-earth-metals salt and ammonium salt; ketone, such as ASECHIRU acetone, methyl acetoacetate, and aceto allyl acetate, is mentioned, and these are independent, or they are combined two or more sorts and used.

[0009]A complex morphogenetic substance is more preferably added 0.3 to 5% 0.1 to 10% to calcium hydroxide. At less than 0.1%, it is almost ineffective, and when 10% is exceeded, there is a tendency which condensation becomes strong too much and it is not not only desirable in cost, but becomes difficult to distribute. Any in the middle of a reaction may be sufficient as the time of addition before a carbonic acid-ized reaction, and it may be added reaction before in the middle of [both] a reaction.

[0010]It flows through carbon dioxide to this milk of lime, and calcium carbonate slurry is generated. 3.5 to 19.3% of milk-of-lime concentration is [the conditions at this time] desirable. At less than 3.5%, since cost becomes high industrially, it is not desirable, and since the calcium carbonate particles generated when 19.3% was exceeded become large, it is not desirable. As for reaction start temperature, 8-30 ** is preferred. Since the calcium carbonate particles undesirably generated when 30 ** was exceeded since cost became high industrially at less than 8 ** become large, it is not desirable. A carbon dioxide flow has preferred 40 - 1800 L/hr. In less than 40 ILhr, since cost will become high industrially if 1800 L/hr is exceeded undesirably, since the generated calcium carbonate particles become large, it is not desirable.

[0011]Like the above, the obtained calcium carbonate slurry is agitated by 20-70 ** of solution temperature for the purpose of distribution of calcium carbonate particles, and the calcium carbonate slurry which is hardly growing is obtained from the diameter of a primary particle of the condensation object of a basis. Since cost will become high industrially if 70 ** is exceeded undesirably, since time requires the temperature at this time for distribution at less than 20 **, it is not desirable. As for churning conditions, not less than 5 rpm is preferred, and they are 5-360 rpm more preferably. Maturing time becomes short so that churning power is large, but if 360 rpm is exceeded, cost becomes high and it is not desirable, and at less than 5 rpm, a maturing period becomes long and is not preferred in cost.

[0012]Judgment whether particles distributed with the manufacturing method of this invention can be checked from the thickening state in the temporality of a particle-size-distribution meter, an electron microscope, and calcium carbonate slurry, etc. Measurement of the specific surface area by the BET method, an electron microscopic picture, etc. are suitable for the check of particles hardly growing in a distributed process, but existing in the state of

particulates on the other hand. the conventional churning and warming -- in the aging method under conditions, by the specific surface area of the particles immediately after carbonic-acid-izing measuring by the BET method, when it is a diameter of a particle about $50 \text{ m}^2/\text{g}$, if particles make maturing distribute, it will be below $20 \text{ m}^2/\text{g}$. That is, by maturing, particles grow and the diameter of a particle becomes large. On the other hand, if it is the method of this invention, even if it uses the conventional aging method, the specific surface area of the BET method can be maintained more than $40 \text{ m}^2/\text{g}$. The dispersion states of the particle are being obtained with the conventional aging method, and a thing more than equivalent. What is necessary is just to use a method suitable timely according to a situation, although there are the method of repeating drying and adding water, etc. removing the wet milling method by the wet mill which uses a glass bead other than the aging method by above-mentioned churning, warming, etc. as a method of distributing an agglomerated particle, the ultrasonic dispersion method, and alkali.

[0013]In the manufacturing method of this invention, as a method of controlling growth of particles further, a phosphorus content substance is added to the calcium carbonate slurry immediately after the above-mentioned combination, it ripens on the above-mentioned conditions, and the method of obtaining the dispersed calcium carbonate slurry without particle growth is mentioned. As a phosphorus content substance said here, phosphoric acid, phosphorous acid, phosphonic acid, those derivatives, those alkali metal salt, alkaline-earth-metals salt, ammonium salt, etc. are mentioned, and these are independent, or are combined two or more sorts, and are used. About 0.01 to 0.6% of the amount of addition is desirable to calcium carbonate. At less than 0.01%, if the particle growth rate of calcium carbonate becomes quick, and particle growth becomes remarkable simultaneously with distribution and 0.6% is exceeded, although particle growth will be suppressed, distribution also tends to become slow and it is not desirable in cost.

[0014][the particulate calcium carbonate obtained by this invention] the thickener of a paint, a sealing material, and a VCM/PVC paste -- the thixotropy grant agent of sol. In a cosmetic material etc., Carrier of the reinforcement agent of rubber, the reinforcement agent of a plastic, the ultraviolet ray absorbent in various fields, the paints for coatings of a coated paper, the paints for printer's ink, and agricultural chemicals, the toner of ink jet paper, etc. are used suitably.

[0015]

[Working example]Although an embodiment and a comparative example are shown below and this invention is explained to it in detail, this invention is not limited only to these embodiments.

[0016]Citrate 3 sodium of concentration was added 8% to calcium hydroxide 10% to the milk of lime of embodiment 1 temperature of 10°C , and 11.8% of concentration, it flowed through

carbon dioxide by the carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, the calcium carbonate slurry with an average particle diameter of 0.44 micrometer of BET specific surface area $50 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at the temperature of 45-50 °C (180 rpm). Reaction conditions and a result are shown in Table 1.

[0017] Citrate 3 sodium of concentration was added 0.5% to calcium hydroxide 10% to the milk of lime of embodiment 2 temperature of 10 °C, and 11.8% of concentration, it flowed through carbon dioxide by the carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, the calcium carbonate slurry with an average particle diameter of 0.34 micrometer of BET specific surface area $28 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at the temperature of 45-50 °C (180 rpm). Reaction conditions and a result are shown in Table 1.

[0018] Citrate 3 sodium of concentration was added 1.0% to calcium hydroxide 10% to milk of lime of embodiment 3 temperature of 10 °C, and 11.8% of concentration, it flowed through carbon dioxide by a carbon dioxide flow of 40 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, a calcium carbonate slurry with an average particle diameter of 0.37 micrometer of BET specific surface area $28 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at temperature of 45-50 °C (180 rpm). Reaction conditions and a result are shown in Table 1.

[0019] Citrate 3 sodium of concentration was added 1.0% to calcium hydroxide 10% to milk of lime of embodiment 4 temperature of 10 °C, and 11.8% of concentration, it flowed through carbon dioxide by a carbon dioxide flow of 40 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, a calcium carbonate slurry with an average particle diameter of 0.37 micrometer of BET specific surface area $40 \text{ m}^2/\text{g}$ was obtained by adding phosphoric acid 0.3% to this calcium carbonate slurry, and agitating for two days at temperature of 45-50 °C (180 rpm). Reaction conditions and a result are shown in Table 1.

[0020] Citrate 3 sodium of concentration was added 3% to calcium hydroxide 10% to milk of lime of embodiment 5 temperature of 10 °C, and 11.8% of concentration, it flowed through carbon dioxide by a carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, M3 type homogenizer of the glory business affairs ground this calcium carbonate slurry by pressure of $570 \text{ kg} / \text{cm}^2$, and a calcium carbonate slurry with an average particle diameter of 0.56 micrometer of BET specific surface area $55 \text{ m}^2/\text{g}$ was obtained. Reaction conditions and a result are shown in Table 1.

[0021] Citrate 3 sodium of concentration was added 1.0% to calcium hydroxide 10% to the milk of lime of embodiment 6 temperature of 10 °C, and 11.8% of concentration, it flowed through

carbon dioxide by the carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, phosphoric acid was added 0.3% to this calcium carbonate slurry, M3 type homogenizer of the glory business affairs ground by the pressure of $570 \text{ kg} / \text{cm}^2$, and the calcium carbonate slur with an average particle diameter of 0.54 micrometer of BET specific surface area $45 \text{ m}^2/\text{g}$ was obtained. Reaction conditions and a result are shown in Table 1.

[0022]It flowed through carbon dioxide by the carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to the milk of lime of embodiment 7 temperature of 10°C , and 11.8% of concentration, and citrate 3 sodium of concentration was added 3% to calcium hydroxide 10% in the stage of 15% of the rate of carbonic-acid-izing. Calcium carbonate was generated by the carbon dioxide flow same after this. Subsequently, the calcium carbonate slur with an average particle diameter of 0.50 micrometer of BET specific surface area $34 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at the temperature of $45\text{--}50^\circ\text{C}$ (180 rpm). Reaction conditions and a result are shown in Table 1.

[0023]Sodium tartrate of concentration was added 3% to calcium hydroxide 10% to the milk of lime of embodiment 8 temperature of 10°C , and 11.8% of concentration, it flowed through carbon dioxide by the carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, the calcium carbonate slur with an average particle diameter of 0.42 micrometer of BET specific surface area $48 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at the temperature of $45\text{--}50^\circ\text{C}$ (180 rpm). Reaction conditions and a result are shown in Table 1.

[0024]A sodium oxalate of concentration was added 3% to calcium hydroxide 10% to milk of lime of embodiment 9 temperature of 10°C , and 11.8% of concentration, it flowed through carbon dioxide by a carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to this slurry, and calcium carbonate was generated. Subsequently, a calcium carbonate slur with an average particle diameter of 0.44 micrometer of BET specific surface area $49 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at temperature of $45\text{--}50^\circ\text{C}$ (180 rpm). Reaction conditions and a result are shown in Table 1.

[0025]It flowed through carbon dioxide by a carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to milk of lime of comparative example 1 temperature of 10°C , and 11.8% of concentration, and calcium carbonate was generated. Subsequently, a calcium carbonate slur with an average particle diameter of 0.55 micrometer of BET specific surface area $12 \text{ m}^2/\text{g}$ was obtained by agitating this calcium carbonate slurry for two days at temperature of $45\text{--}50^\circ\text{C}$ (180 rpm). Reaction conditions and a result are shown in Table 1.

[0026]It flowed through carbon dioxide by a carbon dioxide flow of 1700 L/hr per 1 kg of calcium hydroxide to milk of lime of comparative example 2 temperature of 10°C , and 11.8% of

concentration, and calcium carbonate was generated. Subsequently, M3 type homogenizer ground this calcium carbonate slurry by pressure of $570 \text{ kg} / \text{cm}^2$, and a calcium carbonate slur with an average particle diameter of 0.36 micrometer of BET specific surface area $10 \text{ m}^2/\text{g}$ was obtained. Reaction conditions and a result are shown in Table 1.

[0027]

[Table 1]

	錯体形成 物質の 種類と量	炭酸ガス量 L/hr	誘含有物質の 種類と量	分散方法	分散前の 比表面積 m^2/g	分散後の 比表面積 m^2/g	分散状態 平均粒径 μm
実施例 1	クエン酸 3ナトリウム 3.0%	1700	—	攪拌加温	52	50	0.44
実施例 2	クエン酸 3ナトリウム 0.5%	1700	—	攪拌加温	52	28	0.34
実施例 3	クエン酸 3ナトリウム 1.0%	40	—	攪拌加温	46	28	0.37
実施例 4	クエン酸 3ナトリウム 1.0%	40	燐酸 0.3%	攪拌加温	45	40	0.37
実施例 5	クエン酸 3ナトリウム 3.0%	1700	—	湿式ミル	52	55	0.56
実施例 6	クエン酸 3ナトリウム 1.0%	1700	燐酸 0.3%	湿式ミル	52	45	0.54
実施例 7	クエン酸 3ナトリウム 3.0%	1700	—	攪拌加温	35	34	0.50
実施例 8	酒石酸酸ナトリウム 3.0%	1700	—	攪拌加温	55	48	0.42
実施例 9	シュウ酸ナトリウム 3.0%	1700	—	攪拌加温	53	49	0.44
比較例 1	—	1700	—	攪拌加温	35	12	0.55
比較例 2	—	1700	—	湿式ミル	35	10	0.36

[0028]After carrying out the surface treatment of the fatty acid soda to the calcium carbonate obtained by the example of application 1 above-mentioned embodiments 1-9, and the comparative examples 1-2 7 to 10% to calcium carbonate, it dried by the filter press and the granular material of each calcium carbonate was obtained by dry powder-ization. using these granular materials -- the following combination -- a VCM/PVC paste -- sol was created and the viscosity (viscosity of 2 rpm and 20 rpm) and thixotropy (TI value) were investigated. A result is shown in Table 2.

[0029]90 copies of 30 copies of combination 1 VCM/PVC paste resin (Nippon Zeon 121, ZEON CORPORATION make) DOP(s) calcium carbonate sample 30 copies [0030]90 copies of 30 copies of combination 2 VCM/PVC paste resin (Nippon Zeon 121, ZEON CORPORATION make) DOP(s) calcium carbonate sample 60 copies [0031]

[Table 2]

	配合 1			配合 2		
	粘度 (P)			粘度 (P)		
	2rpm	20rpm	T I	2rpm	20rpm	T I
実施例 1	1630	255	6.35	20000以上	2000以上	——
実施例 2	1200	184	6.49	14700	1930	7.62
実施例 3	1470	225	6.53	12900	1660	7.7
実施例 4	1600	251	6.37	20000以上	2000以上	——
実施例 5	1230	163	7.55	20000以上	2000以上	——
実施例 6	1410	210	6.71	20000以上	2000以上	——
実施例 7	1300	210	6.19	15100	1960	7.70
実施例 8	1310	220	5.95	15000	1910	7.85
実施例 9	1290	197	6.54	14300	1880	7.61
比較例 1	620	92	6.74	4460	590	7.53
比較例 2	720	126	5.71	9700	1400	6.93

[0032] Since the granular material prepared as materials is distributing the calcium carbonate of Embodiments 1-9 by particulates more from the result of Table 2 compared with elegance conventionally, as compared with the granular material of the calcium carbonate of the comparative examples 1-2, high viscosity and thixotropy (TI value) are shown, and it is checked that dispersibility is very good.

[0033]

[Effect of the Invention] The calcium carbonate which distributed the condensation object of calcium carbonate with the state of particulates according to this invention is obtained as above-stated, the thickener of a paint, a sealing material, and a VCM/PVC paste -- it is useful to Carrier of the thixotropy grant agent of sol, the reinforcement agent of rubber, the reinforcement agent of a plastic, the ultraviolet ray absorbent in various fields, the paints for coatings of a coated paper, the paints for printer's ink, and agricultural chemicals, the toner of ink jet paper, a cosmetic material, etc.

[Translation done.]